Bulletin of Electrochemistry 15 (7-8) July-August 1999, pp 300-302

0256-1654/99/$ 3-50

INDIRECT ELECTROCHEMICAL OXIDATION OF O-CHLORO TOLUENE TO O- CHLORO BENZALDEHYDE USING CERIC METHANE SULPHONATE

K JAYARAMAN, V DEVADOSS, A KULANDAI, S THAMIZHARASI
S KRISHNAMOORTHY, R KANAKAM SRINIVASAN AND S CHIDAMBARAM

Central Electrochemical Research Institute, Karaikudi 630 006, INDIA

O-chloro benzaldehyde finds wide applications as chemical intermediates, pharmaceuticals, optical brighteners etc. It is normally produced by acid hydrolysis, but the process generates chlorinated by-products and has poor selectivity. Indirect electrochemical oxidation of o-chloro toluene using ceric mediators offers a facile and clean route for the production of the aldehyde. In this paper results are reported for the oxidation of o-chloro toluene to o-chloro benzaldehyde using ceric methane sulphonate followed by electrochemical regeneration of ceric from cerous thereby making the process cyclic. 60-70% selectivities have been achieved for the chemical oxidation of o- chloro toluene to o-chloro benzaldehyde while the electrochemical regeneration of ceric from cerous proceeds with 70-80% current efficiencies.

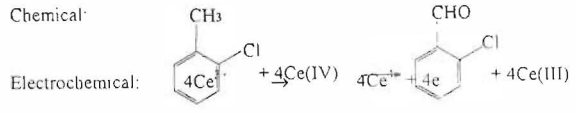
Keywords: O-chloro benzaldehyde, ceric methane sulphonate, indirect electrosynthesis.

INTRODUCTION

O-chloro benzaldehyde finds wide applications in chemical industry as a chemical intermediate and some of its important applications are as brightener in metal plating, intermediate in tear gas production and in voranil synthesis. It is generally produced by the side chain chlorination of toluene followed by hydrolysis. Major disadvantages of the current processs are the low selectivities and highly toxic chlorine effluent. In the present paper results are reported for the potential indirect electrosynthesis of O-chloro benzaldehyde using electrochemically generated ceric mediator in methane sulphonic acid solution.

Even though the use of ceric oxidants in organic synthesis is well known with numerous applications [1], only recently there have been attempts to use these oxidations coupled with electrochemical regeneration and recycling of the ceric oxidant. Cerium (IV) has been reported to be highly selective in the oxidation of some aromatic hydrocarbons [2]. The advantages of using methane sulphonate among various anions are its high stability towards oxidation, high solubility of both cerous and ceric salts and high selectivity for a wide range of organic substrates [3,4]. Preliminary work in this medium was done by Kreh *et al.* [5] and the present authors have recently reported about the indirect electrosynthesis of p-tolualdehyde from p-xylene using ceric methane sulphonate [6]. The objectives of the present studies are to optimize the process conditions for the selective and reproducible synthesis of O-chlorobenzaldehyde from O-chloro toluene with continuous electroregeneration and recycling of the ceric oxidant.

The principle of the process is the electrochemical oxidation of Ce(III) to Ce(IV) in methane sulphonic acid medium and the oxidation of the organic compound in a chemical reactor using Ce(IV) which is reduced to Ce(III) and can be regenerated for recycle. The reactions involved are as follows



EXPERIMENTAL

Solutions of cerous methane sulphonate in methane sulphonic acid were prepared by treating cerous carbonate with calculated quantity of methane sulphonic acid solution to convert cerous carbonate to the cerous salt of methane sulphonic acid and also to maintain the methane sulphonic acid concentration at the desired level. Analysis of ceric content was done by titration with ferrous ammonium sulphate using ferroin as indicator. Analysis of cerous content was accomplished by oxidation to ceric using ammonium

persulphate with silver nitrate catalyst followed by ceric analysis as above.

For electrochemical oxidation of Ce(III) and Ce(IV) batch and flow type electrochemical reactors were used. The batch reactors were provided with flat plate anodes and cathodes and suitable mechanical stirrers for agitation. Flow reactors used in the studies were the commercially available ElectroSyn cell module manufactured by Electro Cell AB of Sweden. Nafion 423 was used as the diaphragm in the cell module.

Chemical reaction of ceric with O-chloro toluene were conducted in an all glass stirred tank reactor provided with reflux condenser and a water bath for heating.

RESULTS AND DISCUSSION

Electrochemical generation of Ce(IV) in methane sulphonic acid medium

Preparative scale experiments were conducted using batch and flow reactors as described in Section 2. Following reactions are involved during electrochemical oxidation of Ce(III) to Ce(IV).

Anode

$$Ce^{3+} \longrightarrow Ce^{4+} + e \qquad (1)$$

$$H_2O \longrightarrow 2H^+ + 0.5O_2 + 2e \qquad (2)$$

Cathode

$$2H^+ + 2e \longrightarrow H_2 \qquad (3)$$

Membrane

$$H^+ [\text{anolyte}] \longrightarrow H^+ [\text{catholyte}] \qquad (4)$$

As seen from reactions [1] and [2], major loss reaction occuring in the electrochemical step is the oxygen evolution occuring at the anode with consequent loss in current efficiency. The main objectives of the studies on electro oxidation of cerous to ceric are to choose a suitable anode material which provides a high current efficiency for the reaction with reasonable current efficiency and is also stable in the reaction environment and is amenable for commercial scale operation. With these objectives in view several electrode materials were examined for ceric generation and the results are reported in Table I. It is seen from the Table I that Platinum and TSIA anodes give high current efficiencies for the reaction. In view of the industrial importance of the reaction, TSIA electrode was chosen for further developmental studies due to its lower cost and availability as an industrial electrode material. Further studies were conducted with TSIA anodes. Studies were conducted to optimise the current density of operation and the results are reported in Table II. It is seen from the Table II that current efficiency decreases with increase in current density and the optimum value for current density is around 5 A/dm^2.

TABLE I: Electro oxidation studies at different anode materials

Experimental conditions		
Cathode	:	Stainless steel
Catholyte	:	Aq-methane sulphonic acid (2 *M*)
Anolyte	:	Ce^{3+} in 2 *M* CJ_3SO_3H
Cell type	:	Divided
Cell divider	:	Nafion cationic membrane
Temperature	:	303 - 308 K

Anode	Input Ce^{3+} (*M*)	C D A/dm^2	Output Ce^{4+} (*M*)	C E (%)
Platinum	0.65	5.0	0.48	70.80
-do-	0.75	7.5	0.54	69.10
TSIA	0.44	5.0	0.42	69.03
TSIA	0.80	3.5	0.66	80.10
DSA–O_2	0.60	5.0	0.43	64.30
DSA–O_2	0.75	5.0	0.63	66.50

Since the concentration of methane sulphonic acid is an important parameter for the chemical oxidation of different organic substrates, electochemical oxidation of Ce^{3+} to Ce^{4+} were conducted with different acid concentrations and the results are reported in Table III. It is seen from the

TABLE II: Effect of current density on current efficiency

Current density (A/dm^2)	Final CERIC in anolyte (*M*)	Current efficiency (%)
2.5	0.54	80.00
3.5	0.57	81.00
5.0	0.62	80.29
6.0	0.45	62.20
7.0	0.31	40.40

Experimental conditions		
Anode	:	TSIA
Cathode	:	S.S
Anolyte	:	0.7 *M* Ce^{3+} 1N 2 *M* MSA
Catholyte	:	A Q MSA

TABLE III: Electrooxidation studies in different acid concentrations

MSA concn (*M*)	Input Ce^{3+} (*M*)	Output Ce^{4+} (*M*)	Current efficiency (%)
1.0	0.700	0.57	80.2
2.0	0.710	0.54	72.5
4.0	0.730	0.64	74.0
5.0	0.620	0.41	60.2
6.0	0.604	0.34	52.9

Experimental conditions
As in Table I and II
C.D. : 5.0 A/dm^2

Table III that there is no significant variation of current efficiencies with acid concentrations and the current efficiency is around 60 to 80% at acid concentrations between 1.0 and 5.0 *M* methanesulphonic acid and the current efficiency decreases to around 53% at 6.0 *M* acid. Thus it is observed that electroregeneration of Ce^{4+} can be effected over a wide range of acid concentrations without loss in current yields.

Chemical oxidation of o-chlorotoluene with Ce^{4+}

Chemical oxidation of o-chloro toluene with Ce^{4+} was conducted in an all glass chemical reactor as described. O-chlorotoluene was taken in dichloroethane medium and was treated with aqueous ceric solution (0.4 to 0.7 *M*). Reaction was conducted till all the ceric was consumed and 4 moles of ceric was taken per mole of o-chlorotoluene charged to the reactor. Studies were conducted initially at a constant acid concentration of 2.0 *M* acid and varying temperatures. From the reaction time and the conversions it was observed that the reaction is favoured at higher temperatures and a temperature of 333 K was chosen as an optimum value between higher reaction rate and minimising the vapour pressure of dichloro ethane. After the completion of the reaction the organic and aqueous phases were separated. The organic phase was vacuum distilled to recover the solvent and the residual liquid after solvent removal was characterised by GC. It was observed from the GC characterisations that the concentration of the o-chlorobenzaldehyde varied from 70 to 80% while the unreacted toluene concentration was between 10 to 40%. The pure aldehyde was obtained by the vacuum fractionation of the heavier residual liquid obtained after the removal of the solvent. The conversion was calculated as the ratio of the product isolated to the reactant converted. The results

TABLE IV: Chemical oxidation of O-chloro toluene to O-chloro benzaldehyde

Acid concn (*M*)	Temperature (K)	CERIC concn in AQ (*M*)	Conversion (%)
2.0	30 ± 2	0.58	40.48
2.0	50 ± 2	0.47	16.59
4.0	50 ± 2	0.73	65.80
4.0	60 ± 2	0.71	85.80
5.0	60 ± 2	0.47	76.80
6.0	60 ± 2	0.41	71.60

Experimental conditions
O-chloro toluene : 1 mole/4 mole CERIC 2.5 - 3 *M* concn in organic phase
Solvent : Dichloro ethane

obtained in the chemical reaction studies are reported in Table IV. It is seen from the Table IV that 4.0 *M* methane sulphonic acid concentration and a temperature of 333 K are the optimum conditions for the reaction. The aqueous phase containing Ce^{3+} was subjected to electro chemical regeneration and the ceric was recycled to the chemical reactor for further oxidations without loss in conversion efficiency.

CONCLUSION

A two stage cyclic process has been established for the indirect electro oxidation of o-chlorotoluene to o-chlorobenzaldehyde. High acid concentrations and temperatures favour the chemical oxidation step and the optimum values are 4.0 *M* methane sulphonic acid and a reaction temperature of around 333 K. Conversion of o-chloro toluene was around 80% under optimum conditions. The regeneration of ceric can be effected with around 65-75% current efficiencies with TSIA anodes in a divided type electrochemical reactor. Compared to the conventional chemical process the electrochemical process is clean and eco-friendly.

REFERENCES

1. T I Ho, *Synthesis*, (1973) 347
2. L Syper, *Tetrahedron Letters*, (1966) 4493
3. R P Kreh, R M Sponitz, J T Lundquist, *Tetrahedron Letters*, **28(10)** (1987) 1067
4. R P Kreh, R M Sponitz and J T Lundquist, *J Org Chem*, **54** (1989) 1526
5. K Jayaraman, V Devadoss, S Krishnamoorthy, R Kanakam Srinivasan and S Chidambaram, Paper communicated to *Bull Electrochem*,